Journal of Metals, Materials and Minerals. Vol.19 No.1 pp.59-65, 2009

Thermoplastic Cassava Starch/Sorbitol-Modified Montmorillonite Nanocomposites Blended with Low Density Polyethylene: Properties and Biodegradability Study

Saowaroj CHUAYJULJIT*, Suwasin HOSILILAK and Anankran ATHISART

Department of Materials Science, Faculty of Science, Chulalongkorn University,
Phyathai Rd., Pathumwan, Bangkok 10330, Thailand
National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials,
Chulalongkorn University, Phyathai Rd., Pathumwan, Bangkok 10330, Thailand

Received Apr. 30, 2009
Accepted May 10, 2009

Abstract

The objective of this research paper is to prepare environmentally friendly plastic materials from biodegradable cassava starch, montmorillonite (MMT) and low density polyethylene (LDPE). MMT was first modified by sorbitol via a solid state method. Results from X-ray diffraction (XRD) indicated that sorbitol molecules were intercalated in between MMT layers along 001 direction. Cassava starch was plasticized with sorbitol and formamide on a two-roll mill to obtain thermoplastic starch (TPS). The TPS/modified-MMT nanocomposites were prepared by means of melt blending of TPS with various amounts of MMT (0, 2, 4, and 6 phr). XRD and transmission electron microscopy (TEM) results showed that the nanocomposites formed were all exfoliated. The prepared nanocomposites were subsequently blended with a mixture of 80 LDPE/20 PE wax on a two-roll mill followed by a compression molding machine. The obtained polymer blends were examined for their impact and flexural strength, water absorption, morphology and biodegradability. The mechanical properties of LDPE were improved by incorporating 10 phr of TPS nanocomposite that contained MMT 2 phr and gained the highest impact and flexural strengths of 2900 J m^{-2} and 17 N m^{-2}, respectively. The scanning electron micrographs displayed that the TPS nanocomposites with a high loading of starch and MMT exhibited poor distribution in PE matrix. Water absorption and biodegradability of the nanocomposites were enhanced with the increasing amount of cassava starch. However, silicate layers with high aspect ratio could serve as a barrier and reduce the water-uptake ability of these materials.

Key words : Cassava starch, Montmorillonite, Nanocomposite, LDPE, Impact and flexural strength, Biodegradability

Introduction

One of today's serious global problems is the management of the steadily increasing amount of solid waste. Tremendous quantities of polymers, mainly polyolefins (e.g. polyethylene, polypropylene) are produced and discarded into the environment, ending up as wastes that do not degrade spontaneously. Some polymer products have a short useful life, in many cases of less than two years. They are consumed and discarded into the environment when their utilization ceases. The petroleum-based polymers were developed for durability and resistance to all forms of degradation. With developing environmental ecological awareness, biodegradable plastics are proposed as one of many strategies to alleviate the environmental impact of petroleum-based plastics and are gaining public interest. They are designed to be easily degraded by the enzymatic action of living microorganisms such as bacteria, yeasts and fungi.(1) In contrast to synthetic polymers, natural polymers are good base materials for producing inexpensive, rapid degradable plastics. The use of biodegradable materials based on renewable resources can help reduce the percentage of plastics in industrial and household wastes. Therefore, several considerable efforts have been made to accelerate the biodegradability of polymeric materials by replacing some or all of the synthetic polymers with natural polymers in many applications in order to minimize the environmental problems caused by plastic wastes.(1-4)

---

*Corresponding author Tel.: +66 2218 5061; Fax.: +66 2218 5561
E-mail: schuayjuljit@yahoo.com

Starch is one of the main natural polymers used in the production of biodegradable materials because of its renewability, biodegradability, wide availability and low cost.(2,4-6) However, the starch presents some drawbacks, such as the strong hydrophilic behavior and poorer mechanical properties when compared to synthetic polymers.(2,5,7) It is predominantly water-soluble and cannot be processed by melt-based routes because it decomposes before melting.(8,9) To improve the mechanical and barrier properties of the starch composites at the same time, a small amount of inorganic nanofillers is commonly added to a polymer matrix. The clay, montmorillonite (MMT), is one of the attractive nanofillers utilized due to its high aspect ratio of width/thickness, in an order of 10-1000. Indeed, for very low amounts of nanoparticles, the total interface between polymer and silicate layers is much greater than that in conventional composites.(10) In general, the clay needs to be modified in order to enlarge the interlayer distance. Ma, *et al.* prepared sorbitol-modified montmorillonite, which was added into the thermoplastic starch (TPS) to obtain nanocomposites by dual-melt extrusion process.(6) Sorbitol is an alcohol sugar widely used in the food industry, not only as a sweetener, but also as a humectant, texturizer, and softener.(7) In this study, cassava starch was mixed with montmorillonite to obtain starch nanocomposites in order to improve its mechanical properties and water resistance. However, the starch was first plasticized under heating to obtain thermoplastic starch, giving rise to a continuous phase in the form of a viscous melt which can be processed by conventional plastic processing technique. In general, plasticizers used include polyols such as glycerol, glycol, xylitol and sorbitol. Plasticizers containing amide groups such as urea, formaldehyde and acetamide or a mixture of plasticizers have also been studied.(11) In this experiment, the plasticizers used for preparing TPS were sorbitol and formamide.

The objective of this paper is to prepare biodegradable plastics of low density polyethylene (LDPE) using polyethylene wax (PE wax) with a molecular weight of 1500±500 as a processing aid. Thermoplastic cassava starch/sorbitol-modified MMT nanocomposites with various amounts of MMT were incorporated into the blend of 100 LDPE/80 PE wax in order to enhance the mechanical properties and biodegradability of the blend. The structure and morphology of the samples were investigated by X-ray diffractometer and transmission electron microscope. The impact strength, flexural strength and biodegradability were also examined.

Materials and Experimental Procedures

Materials

Cassava starch was supplied by Thaiwa Company. Montmorillonite (MMT) was acquired from the Metallurgy and Materials Science Research Institute, Chulalongkorn University. Low density polyethylene, LD1902F with a melt flow index of 2 g/10 min and PE wax were donated by Thai Polyethylene Company. Sorbitol and formamide were purchased from Ajax Finechem Company. All materials were used as received without further purification.

Preparation of Thermoplastic Cassava Starch/ Sorbitol-Modified MMT Nanocomposites

Thermoplastic cassava starch/sorbitol-modified MMT nanocomposites were prepared in two steps. In the first step, MMT was modified via solid state method using sorbitol. MMT was premixed manually with sorbitol at a weight ratio of 1:2 at 100°C for 1 min in accordance with a previous study of Ma, *et al.*(2007) The mixture was further stirred vigorously by a high speed mixer at 3000 rpm for 2 min. The obtained sorbitol-modified MMT was dried in an oven and then ground into powder. In the second step, cassava starch (100 g) sorbitol and four different modified-MMT contents (0, 6, 12 and 18 g) were premixed in a high speed mixer at 3000 rpm for 2 min. Formamide (10 g) was added and mixed (3000 rpm for 2 min).(6) After that, the resulting mixtures were processed on a two-roll mill at 150°C. The compositions of TPS/sorbitol-modified MMT nanocomposites are listed in Table 1. The gross amounts of sorbitol in the nanocomposites were constant at 20 g and the MMT contents in the nanocomposites were 0, 2, 4 and 6 parts per hundred of starch. The obtained nanocomposites were then ground into powder.

Table 1. Composition of the blends.

Sample codes	MMT (phr)	MMT-Sorbitol (1:2)(g)	Cassava starch (g)	Formamide (g)	Sorbitol (g)
TPSM-0	0	0	100	10	20
TPSM-2	2	6	100	10	16
TPSM-4	4	12	100	10	12
TPSM-6	6	18	100	10	8

Blend of TPS/Modified MMT Nanocomposites with LDPE

LDPE was firstly blended with PE wax at a weight ratio of 80:20. The blend was then mixed with TPS/modified MMT nanocomposites (TPSM-0, TPSM-2, TPSM-4 and TPSM-6) in the amount of 10, 20 and 30 phr (based on the amount of LDPE/PE wax) on a two-roll mill until the mixtures were evenly mixed. The mixtures were then taken out and molded into sheets by a hot press at 150°C. The sheets were prepared for characterization and properties measurement.

Characterization

X-Ray Diffraction (XRD)

MMT, modified-MMT and TPS/modified-MMT nanocomposites were examined at room temperature by a Bruker AXS D8 X-ray diffractometer, operated at 40 kV and 40 mA, equipped with CuK_α radiation at a wavelength of 0.1542 nm. The experiments were performed in a 2θ range of 1-10° with a scan rate of 2°/min. The basal spacing of the silicate layer (d_{001}) was calculated by using Bragg's equation, $\lambda = 2d \sin\theta$, where λ is the wavelength of the X-ray radiation used, d is the spacing between diffractional lattice planes, and θ is the measured diffraction angle.

Transmission Electron Microscopy (TEM)

Transmission electron micrographs of TPS/modified-MMT nanocomposites were obtained with a Jeol JS-M2010 using an accelerating voltage of 200 kV. The specimen was prepared using a Leica Ultracut microtome equipped with a cryo-chamber. A thin section was cut with a diamond knife at -110°C.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs of the nanocomposites were obtained using a Jeol JS-M6480 with an acceleration voltage of 15 kV and magnification of 500×. The samples were cooled in liquid nitrogen, and then fractured. The fracture surfaces were sputter coated with a thin layer of gold prior to SEM examination.

Mechanical Testing

Impact test was measured according to ASTM D256-06 on a GOTECH GT-7045-MDH impact tester. Notched Izod impact specimens were cut from the nanocomposite sheets with dimensions of $12.7 \times 63.5 \times 3$ mm^3 with a V-shape notch.

The flexural strength of the nanocomposites was measured by a three-point loading system according to ASTM D790 using a universal testing machine (Lloyd 500). The load cell capacity and the test speed were 100 kN and 1.1 mm/min, respectively.

Water Absorption

The water absorption was determined using a sample sheet with 16 × 48 × 1 mm dimensions. The sample was oven-dried at 50°C for 24 h, cooled in a desiccator, and immediately weighed to obtain the initial weight (W_0). The sample was placed in a container of distilled water for 1, 5 and 10 days. After soaking for the specified interval, the sample was then removed from the water, gently dried by wiping with a clean cloth, and weighed immediately to obtain the weight of sample after exposure to water absorption (W_1). The sample was placed back in water after each measurement. The percent water absorption was calculated from the following equation:

$$\%\ \text{Water absorption} = [(W_1 - W_0)/W_0] \times 100$$

Soil Burial Test

Biodegradation of the samples was studied by the soil burial method. Rectangular samples with 25 × 25 × 1 mm dimensions were dried in a desiccator until their weights became constant (W_2). These samples were then buried in the test soil at a depth of 15-20 cm from the surface for four weeks. The soil was put into the preparation box (15 × 15 × 20 cm) and maintained at approximately 25 % (w/w) moisture content. After two weeks, the samples were carefully washed with water and dried until their weight became constant (W_3). The percent weight loss was calculated from the following equation:

$$\%\ \text{Weight loss} = [(W_2 - W_3)/W_2] \times 100$$

Results and Discussion

XRD Patterns

To evaluate sorbitol and starch intercalation in MMT layers, XRD analyses were performed. The

X-ray patterns of raw MMT, sorbitol-modified MMT and TPS/sorbitol-modified MMT nanocomposites are shown in Figure 1. The XRD patterns reveal that when MMT was modified with sorbitol, the interlayer distance was enlarged from 1.254 to 1.839 nm, which indicates that sorbitol had intercalated into the layers of MMT, and the modified-MMT was successfully prepared through the solid state method. The advantage of the solid state method is to diminish environmental pollution caused by the organic solution and the production of waste water during the modification process.(6,12) However, the diffractograms of the TPS/sorbitol-modified MMT nanocomposites show no noticeable peak in the 2θ range of 0-10°. The disappearance of the diffraction peaks implies that the silicate layers are homogeneously delaminated and randomly dispersed in the TPS at the nanometer level. Apparently thus, exfoliated nanocomposites were formed. To help confirm these results we performed TEM analysis.

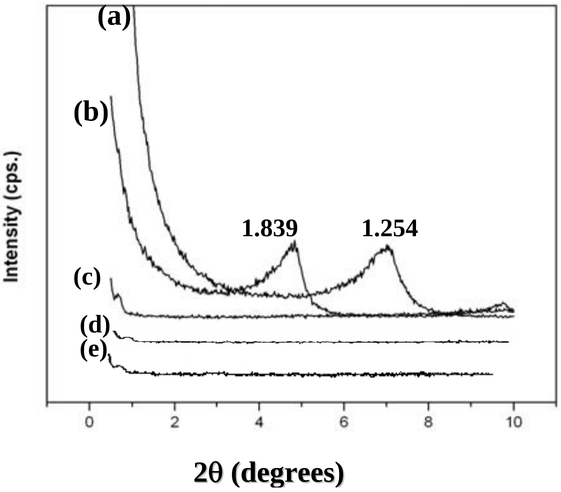

Figure 1. XRD patterns of (a) MMT, (b) sorbitol-modified MMT, (c) TPSM-2, (d) TPSM-4 and (e) TPSM-6.

TEM

Though XRD is an useful tool to study the *d*-spacing in nanocomposites, but it does not constitute a stand alone technique to study their morphology.(13) The use of TEM in combination with XRD for the identification of an exfoliated nanocomposite is recommended. Thus, the TPS/sorbitol-modified MMT nanocomposites were examined by TEM, and representative micrographs are shown in Figure 2. The dark areas are the MMT layers dispersed in the TPS. The TEM micrographs appear to support the XRD data, showing that the exfoliated nanocomposites are formed.

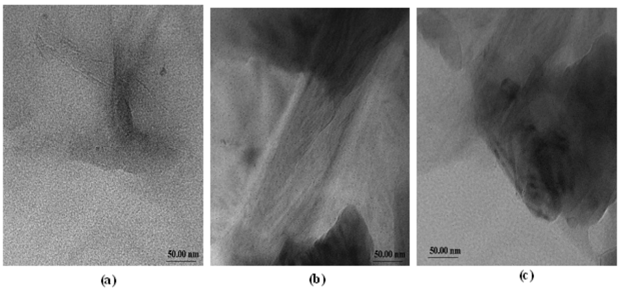

Figure 2. TEM micrographs of (a) TPSM-2, (b) TPSM-4 and (c) TPSM-6.

SEM

Scanning electron micrographs of impact-fractured surfaces of LDPE/PE wax blended with TPS/modified-MMT nanocomposites (TPSM-0, TPSM-2, TPSM-4, and TPSM-6) at 0, 10, 20 and 30 phr are shown in Figures 3-5. It can be seen that the distribution of TPS/modified-MMT nanocomposites in LDPE/PE wax matrix is worse with increasing amount of cassava starch and MMT in the nanocomposites. This is due to the hydrophilic nature of starch and MMT that leads to poor adhesion (miscibility) with LDPE and PE wax, which are hydrophobic in nature. Thus, at high loading of starch and MMT, micrographs show coarse holes of various sizes created due to the partial removal of loosely embedded starch granules. This may lead to poor mechanical properties of the blends. On the other hand, the corresponding blend with no such holes is expected to exhibit better mechanical properties.

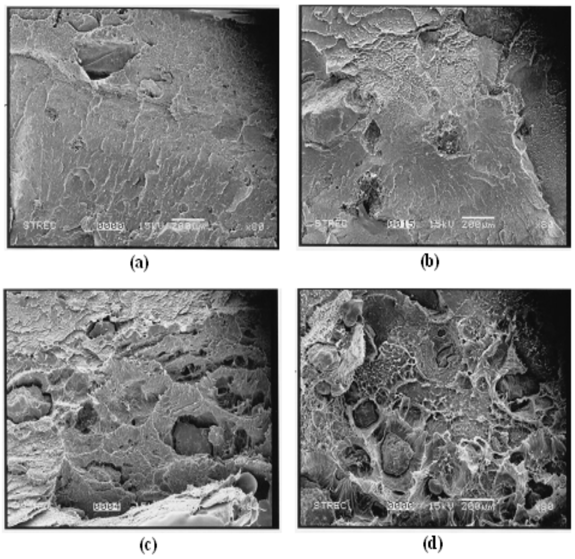

Figure 3. SEM micrographs of the blends of (a) 80 LDPE/20 PE wax/10 TPSM-0, (b) 80 LDPE/20 PE wax/10 TPSM-2, (c) 80 LDPE/20 PE wax/10 TPSM-4, (d) 80 LDPE/20 PE wax/10 TPSM-6.

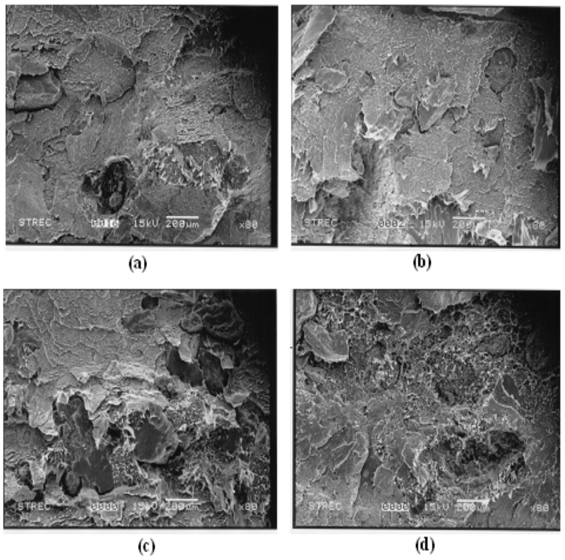

Figure 4. SEM micrographs of the blends of (a) 80 LDPE/20 PE wax/20 TPSM-0, (b) 80 LDPE/20 PE wax/20 TPSM-2, (c) 80 LDPE/20 PE wax/20 TPSM-4, (d) 80 LDPE/20 PE wax/20 TPSM-6.

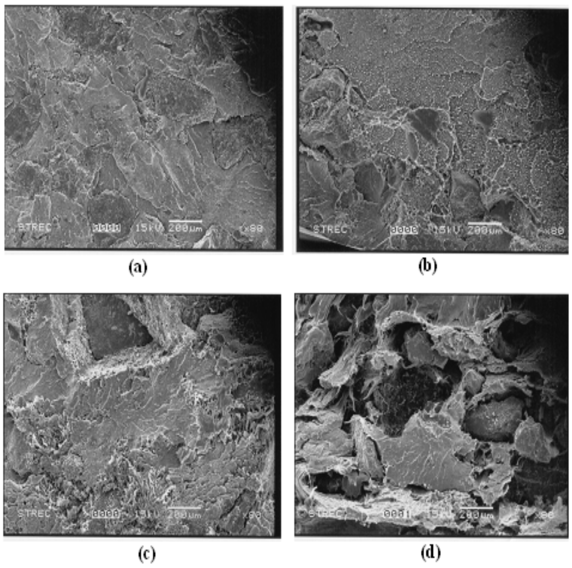

Figure 5. SEM micrographs of the blends of (a) 80 LDPE/20 PE wax/30 TPSM-0, (b) 80 LDPE/20 PE wax/30 TPSM-2, (c) 80 LDPE/20 PE wax/30 TPSM-4, (d) 80 LDPE/20 PE wax/30 TPSM-6.

Mechanical Properties

Figure 6 illustrates the plots of impact strength vs. the amount of TPS/modified-MMT nanocomposites in the blends (10, 20 and 30 phr) and weight percentage of MMT in the nanocomposites (0, 2, 4 and 6 phr). The impact strength of all the blends decreased with increasing nanocomposite content, indicating that cassava starch behaved as non-reinforcing filler. This may be due to the low interfacial interaction between starch and PE, which would lead to mechanical rupture at the blend interface. However, this property improves by the addition of MMT at 2 phr when compared with the blend without MMT. Although 2 wt% of MMT brings increased impact strength, this effect decreases with increasing TPS concentration. The blend of 80 LDPE/20 PE wax/10 TPSM-2 exhibits the highest impact strength (2900 J m^{-2}). Further increase in MMT loading causes the impact strength of the blends to decrease owing to the aggregation of TPS and modified-MMT that leads to poor adhesion with PE. The results are in agreement with SEM observations.

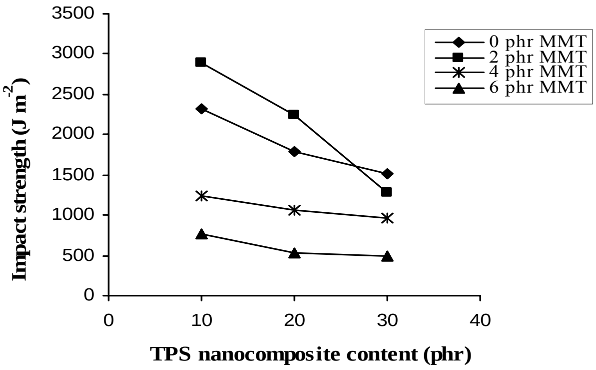

Figure 6. Impact Strength of the Blends.

Figure 7 clarifies that the trend for flexural strength is similar to that observed for impact strength. The blend of 80 LDPE/20 PE wax/10 TPSM-2 exhibits the highest flexural strength (17 N m^{-2}). It can be concluded that the properties of PE blends decreased because of poor interfacial adhesion strength.

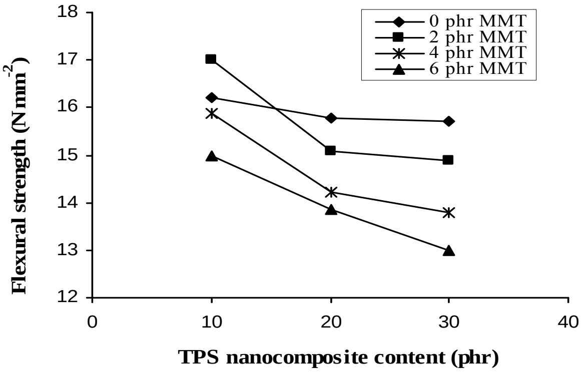

Figure 7. Flexural strength of the blends.

Water Absorption

The effects of cassava starch and MMT on water absorption of the blends after immersion in water for different periods of time (1, 5 and 10 days) are summarized in Table 2. It can be seen that the water absorption of the samples increased with the increasing incorporation of starch. Since PE possesses a hydrophobic feature, the water absorption of the samples is mainly due to the starch. The blend with higher water absorption is usually more prone to microorganism attack. This is likely to allow microorganisms, such as bacteria and fungi, access to the inferior of the matrix using water as a medium; the result implies that the samples with higher starch contents would exhibit the potential for better biodegradability. However, it can be noticed that the samples with higher loading of MMT have relatively lower water absorption. The result can be attributed to the fine dispersion of silicate layers within the nanocomposites. The high aspect ratio of silicate layers could increase the contact surface area between the filler and the matrix. The tortuosity of the diffusion path served as a barrier for the water to diffuse inside the samples.(3,10,14) Therefore, samples with high loading of MMT exhibit reasonably good water resistance compared to LDPE/TPS blends. Thus, blends containing a high loading of starch could be made more water resistant.

Table 2. Water absorption of the blends.

Samples	**Percentage of water absorption**		
	1 day	**5 days**	**10 days**
80 LDPE/20 PE wax	0.004	0.007	0.017
80 LDPE/20 PE wax/10 TPSM-0	0.214	0.244	0.338
80 LDPE/20 PE wax/20 TPSM-0	0.352	0.370	1.229
80 LDPE/20 PE wax/30 TPSM-0	0.438	0.553	1.881
80 LDPE/20 PE wax/10 TPSM-2	0.239	0.249	0.305
80 LDPE/20 PE wax/20 TPSM-2	0.284	0.343	0.583
80 LDPE/20 PE wax/30 TPSM-2	0.407	0.523	0.646
80 LDPE/20 PE wax/10 TPSM-4	0.157	0.174	0.196
80 LDPE/20 PE wax/20 TPSM-4	0.247	0.294	0.327
80 LDPE/20 PE wax/30 TPSM-4	0.339	0.455	0.618
80 LDPE/20 PE wax/10 TPSM-6	0.025	0.048	0.087
80 LDPE/20 PE wax/20 TPSM-6	0.033	0.101	0.169
80 LDPE/20 PE wax/30 TPSM-6	0.055	0.349	0.488

Soil Burial Test

The biodegradability of TPS/sorbitol-modified MMT nanocomposites blended with LDPE was estimated using soil burial method. Table 3 shows the biodegradation of the blends containing different amounts of TPS/modified-MMT nanocomposites in soil by monitoring starch removal. The dry weight loss of the samples after burial in soil for two weeks was determined. The weight loss observed at each time point over the two weeks was larger with increasing starch content in the blend. This suggests that the microorganisms consume starch and create pores in the PE matrix. However, the rate of weight loss does not only depend on the starch content, but also on the MMT content. This is in good agreement with the result of water absorption described earlier.

Table 3. Weight loss of the blends after soil burial.

Samples	**Percentage of weight loss**			
	4 day	**7 days**	**10 days**	**14 days**
80 LDPE/20 PE wax	0.002	0.014	0.033	0.090
80 LDPE/20 PE wax/10 TPSM-0	0.221	0.246	0.266	0.315
80 LDPE/20 PE wax/20 TPSM-0	0.233	0.283	0.322	0.367
80 LDPE/20 PE wax/30 TPSM-0	0.271	0.343	0.379	0.465
80 LDPE/20 PE wax/10 TPSM-2	0.198	0.225	0.264	0.298
80 LDPE/20 PE wax/20 TPSM-2	0.204	0.244	0.331	0.396
80 LDPE/20 PE wax/30 TPSM-2	0.243	0.336	0.351	0.422
80 LDPE/20 PE wax/10 TPSM-4	0.104	0.221	0.244	0.291
80 LDPE/20 PE wax/20 TPSM-4	0.187	0.264	0.281	0.394
80 LDPE/20 PE wax/30 TPSM-4	0.232	0.250	0.347	0.416
80 LDPE/20 PE wax/10 TPSM-6	0.032	0.087	0.142	0.228
80 LDPE/20 PE wax/20 TPSM-6	0.116	0.131	0.165	0.197
80 LDPE/20 PE wax/30 TPSM-6	0.207	0.242	0.316	0392

Conclusion

Biodegradable plastics from cassava starch, montmorillonite and LDPE were successfully produced through a melt mixing process. Cassava starch is a cheap raw material, abundant, renewable, and readily available ubiquitously and very versatile in terms of chemical and physical modification, whilst MMT is natural, but although neither renewable nor cheap, is used in a very small amount. Plastic materials with acceptable biodegradation and mechanical properties were achievable by adequately adjusting the composition of the blends. Overall, 80 LDPE/20 PE wax/10 TPSM-2 blend showed optimum mechanical properties. However, the biodegradable polymers with fast degradation rate may exhibit unsatisfactory mechanical properties and limit their use in wet environments. One possible solution to this problem is to reduce the water absorption bility of these materials by using starch/MMT nanocomposites.

Acknowledgements

The authors gratefully acknowledge the Faculty of Science, the Metallurgy and Materials Science Research Institute and the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, for financial, material and instrument support. We also thank Thai Polyethylene Company and Thaiwa Company for supply of materials.

References

1. Avella, M., De Vlieger, J.J., Errico, M.E., Fischer, S., Vacca, P. and Volpe, M.G. 2005. Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chem.* **93(3)** : 467-474.

2. Thakore, I.M., Desai, S., Sarawade, B.D. and Devi, S. 2001. Studies on biodegradability, morphology and thermomechanical properties of LDPE/modified starch blends. *Eur. Polym. J.* **37(1)** : 151-160.

3. Chiu, F.C., Lai, S.M. and Ti, K.T. 2009. Characterization and comparison of metallocene-catalyzed polyethylene/thermoplastic starch blends and nanocomposites. *Polym. Test.* **28(3)** : 243-250.

4. Huang, C.Y., Roan, M.L., Kuo, M.C. and Lu, W.L. 2005. Effect of compatibiliser on the biodegradation and mechanical properties of high-content starch/low-density polyethylene blends. *Polym. Degradation. Stab.* **90(1)** : 95-105.

5. Tang, S., Zou, P., Xiong, H. and Tang, H. 2008. Effect of nano-SiO_2 on the performance of starch/polyvinyl alcohol blend films. *Carbohyd. Polym.* **72(3)** : 521-526.

6. Ma, X., Yu, J. and Wang, N. 2007. Production of thermoplastic starch/MMT-sorbitol nanocomposites by dual-melt extrusion processing. *Macromol. Mater.Eng.* **292(6)** : 723-728.

7. Park, H.R., Chough, S.H., Yun, Y.H. and Yoon, S.D. 2005. Properties of starch/PVA blend films containing citric acid as additive. *J. Polym. Environ.* **13(4)** : 375-382.

8. Carvalho, A.J.F., Job, A.E., Curvelo, A.A.S. and Gandini, A. 2003. Thermoplastic starch/ natural rubber blends. *Carbohyd. Polym.* **53(1)** :1-5.

9. Mano, J.F., Koniarova, D. and Reis, R.L. 2003. Thermal properties of thermoplastic starch/ synthetic polymer blends with potential biomedical applicability. *J. Mater. Sci.: Mater. Med.* **14(2)** : 127-135.

10. Choudalakis, G. and Gotsis, A.D. 2009. Permeability of polymer/clay nanocomposites: A review. *Eur. Polym. J.* **45(4)** : 967-984.

11. Yang, J.H., Yu, J.G. and Ma, X.F. 2006. Preparation and properties of ethylenebisformamide plasticized potato starch (EPTPS). *Carbohyd Polym.* **63(2)** : 218-223.

12. Mingliang, G. 2009. Preparation and properties of polypropylene/clay nanocomposites using an organoclay modified through solid state method. *J. Reinf. Plast. Compos.* **28(1)** : 5-15.

13. Fedullo, N., Sorlier, E., Sclavons, M., Bailly, C., Lefebvre, J.M. and Devaux, J. 2006. Polymer-based nanocomposites: Overview, applications and perspectives. *Prog. Org. Coatings.* **58(2-3)** : 87-95.

14. Giannakas, A., Spanos, C.G., Koirkoumelis, N., Vaimakis, T. and Ladavos, A. 2008. Preparation, characterization and water barrier properties of PS/organo-montmorillonite nanocomposites. *Eur. Polym. J.* **44(12)** : 3915-3921.